PATENT SPECIFICATION

(11) **1 437 191**

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(21) Application No. 42444/73 (22) Filed 10 Sept. 1973

(31) Convention Application No. 151 412

(32) Filed 11 Sept. 1972 in

(33) Canada (CA)

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(19)

(54) PROCESS FOR THE PRECIPITATION OF METAL CARBONATES

(71) We, THE INTERNATIONAL NICKEL COMPANY OF CANADA, LIMITED, a Canadian Company, of Copper Cliff, Ontario, Canada, do hereby declare the

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[column fragments:] ions / ounts / itions / basic 50 / l and / ically / iation / bath, / there 55 / ls in / filter- / . low / sinter / sence 60 / nt in / nate) / er by / nates / le to 65 / ; and

carbonate solution or *vice versa*, stirring the two solutions together, allowing the precipitate thus formed to settle and decanting or filtering off the supernatant liquid. This reaction, as applied to sulphate solutions and using sodium carbonate, can be represented as follows: 30

$$MeSO_4 + Na_2CO_3 + (n+x)H_2O$$

$$—(Me n OH)_2 . 1—n) MeCO_3 . xH_2O + Na_2SO_4 + nCO_2,$$

wherein Me represents nickel, cobalt, copper or zinc. Generally, this process is difficult to operate using large amounts of material. The precipitate formed is usually very finely divided and settles and filters slowly. Furthermore, the finely divided precipitate is very difficult to wash free of impurities. 35, 40

Another difficulty in the precipitation of basic metal carbonates is that the precipitates

the pH and temperature of the precipitation metal carbonates, e.g. nickel and cobalt carbonate and basic carbonate can be obtained which are easily filterable. 70

The present invention accordingly provides a process for preparing a precipitate of carbonate or basic carbonate of nickel, cobalt, copper or zinc in which a stream of a first aqueous solution of a water-soluble salt of nickel, cobalt, copper or zinc is mixed substantially continuously in an agitated reaction zone at a temperature in the range of from 85 to 95° C. and at a pH in the range of from 7.4 to 8.0 with a stream of a second aqueous solution of an alkali metal carbonate, an alkali metal carbonate and hydroxide, or an alkali metal carbonate and bicarbonate, and the resulting precipitate is recovered, the amount of alkali metal carbonate and hydroxide or bicarbonate, expressed in terms of the alkali metal, being that required to use up any free acid in the salt solution and 75, 80, 85, 90

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(54) PROCESS FOR THE PRECIPITATION OF METAL CARBONATES

(71)   We, THE INTERNATIONAL NICKEL COMPANY OF CANADA, LIMITED, a Canadian Company, of Copper Cliff, Ontario, Canada, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to precipitation of metal basic carbonates and, more particularly, to precipitation of nickel and/or cobalt carbonate and basic carbonate in a form which readily settles to provide a high solids content in the underflow and which is readily filterable.

In the recovery of metals, e.g. nickel, cobalt, zinc and copper, from aqueous solution, particularly in hydrometallurgical processes, and in precipitating nickel and/or cobalt in relatively pure form, it is desirable to precipitate the dissolved metal as the carbonate or basic carbonate. Conventionally, the formation of basic carbonate is accomplished by introducing a metal salt-containing solution into a carbonate solution or *vice versa*, stirring the two solutions together, allowing the precipitate thus formed to settle and decanting or filtering off the supernatant liquid. This reaction, as applied to sulphate solutions and using sodium carbonate, can be represented as follows:

$$MeSO_4 + Na_2CO_3 + (n+x)H_2O$$

$$\rightarrow (Me \; n \; OH)_2 . 1-n) \; MeCO_3 . \\ xH_2O + Na_2 \; SO_4 + nCO_2,$$
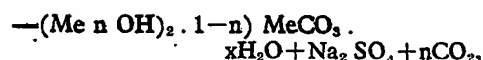
wherein Me represents nickel, cobalt, copper or zinc. Generally, this process is difficult to operate using large amounts of material. The precipitate formed is usually very finely divided and settles and filters slowly. Furthermore, the finely divided precipitate is very difficult to wash free of impurities.

Another difficulty in the precipitation of basic metal carbonates is that the precipitates are not specific compounds. Essentially, as indicated by the above equation, the precipitates consist of metal ion, e.g. nickel or cobalt ion, combined with carbonate and hydroxyl ions and water of constitution, the relative amounts of which depend upon the precise conditions of precipitation. If the nickel or cobalt basic carbonate is to be thermally decomposed and reduced to metal, it need not be so chemically reactive as is desirable for rapid neutralisation of an acid solution, e.g. an electrowinning bath, but it should be rapid settling and there should be a high percentage of solids in the underflow and it should be readily filterable and have low cake moisture and low sulphate content. When nickel or cobalt sinter is made by reducing oxide in the absence of siliceous refractory, sodium ion present in the oxide precursor (i.e. basic carbonate) can generally be removed from the sinter by leaching. Precipitated metal basic carbonates should be readily settleable and filterable to avoid difficulty and expense in handling and production.

It has now been found that by controlling the pH and temperature of the precipitation metal carbonates, e.g. nickel and cobalt carbonate and basic carbonate can be obtained which are easily filterable.

The present invention accordingly provides a process for preparing a precipitate of carbonate or basic carbonate of nickel, cobalt, copper or zinc in which a stream of a first aqueous solution of a water-soluble salt of nickel, cobalt, copper or zinc is mixed substantially continuously in an agitated reaction zone at a temperature in the range of from 85 to 95° C. and at a pH in the range of from 7.4 to 8.0 with a stream of a second aqueous solution of an alkali metal carbonate, an alkali metal carbonate and hydroxide, or an alkali metal carbonate and bicarbonate, and the resulting precipitate is recovered, the amount of alkali metal carbonate and hydroxide or bicarbonate, expressed in terms of the alkali metal, being that required to use up any free acid in the salt solution and

additionally from 100 to 127% of the theoretical stoichiometric amount required to precipitate the pure normal carbonate.

To maintain the pH of the reaction zone within the above range the separate streams entering the reaction zone should be metered so as to introduce the carbonate solution and the metal salt-containing solution continuously into the reaction zone in those proportions. The reaction zone is preferably maintained at a temperature of about 90° C. and the pH is preferably maintained in the range 7.6 to 7.8 and most advantageously substantially constant.

The soluble salt of nickel, cobalt, copper or zinc is preferably the sulphate and the process is particularly applicable to the treatment of solutions of salts of nickel, cobalt or mixtures thereof.

Vigorous agitation of the reaction zone and thorough mixing of the feeds of metal salt-containing solution and carbonate solution are desirable to promote particle growth. It has been found that, for example, introducing the feeds through opposite sides of a reaction chamber adjacent to the periphery of a turbine impeller having a peripherical speed of about 3 metres per second provides adequate dispersion for 2.5 litres of slurry. As a general rule when employing a cylindrical reaction zone adequate agitation is provided by an axially mounted, baffled turbine agitator having a flat-bladed impeller of diameter about one-third to about one-half the diameter of the reaction zone. Such an impeller should generally be powered to provide in the reaction zone substantially the same agitation as would be provided by a similar impeller powered by 0.1 horsepower in a 2.5 litre reaction zone. Generally, a minimum power of about 1 horsepower is appropriate for a reaction zone of 650 litres and 60 horsepower is appropriate for a reaction zone of about 40,000 litres. These powers are of course subject to change caused by different apparatus configurations, concentration of feeds, and solids content of the slurry formed by the reaction.

Maintenance of a pH of 7.4 to 8.0 in the reaction zone generally requires the continuous introduction of a small excess of alkali. When alkali metal carbonate is used, this excess is generally about 25% of the stoichiometrical amount required to react with the metal salt in a neutral solution. The excess of alkali required may be reduced by substitution of an equivalent amount of alkali metal hydroxide for part of the carbonate; by aeration of the reaction zone during precipitation, or of the resulting slurry, with air or other non-reactive gas; or by any two or all of these means, together.

Up to 50 mole % of the carbonate may be replaced by hydroxide, so that the molar ratio of hydroxide to carbonate is up to 2:1.

Aeration acts in the same way as substitution of hydroxide for carbonate. This is because aeration increases the loss to the atmosphere of carbon dioxide produced during the precipitation. In the pH range of 7.4 to 8.0 carbon dioxide in solution may be considered as being present as sodium bicarbonate, and the loss of carbon dioxide to the atmosphere causes a shift towards completion of the decomposition of the alkali metal bicarbonate to alkali metal hydroxide and carbon dioxide, viz.

$$NaHCO_3 \rightleftharpoons NaOH + CO_2$$
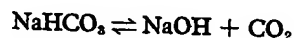
The loss of carbon dioxide to the atmosphere thus increases the amount of hydroxide present and increases the basicity of the aqueous medium. It has been found that, in the case of a metal salt solution which requires an approximately 25% excess of alkali metal carbonate over the true stoichiometrical requirement to maintain the pH of the reaction zone within the above range of 7.4 to 8.0, aeration reduces the excess needed to maintain the same pH to approximately 12%, thus reducing reagent cost.

Aeration and substitution of hydroxide for carbonate results, as would be expected, in a lower carbon dioxide content in the precipitate. Generally, the lower the carbonate content of the precipitate, the lower is the alkali metal content of the precipitate. Conversely, as the carbonate content of the precipitate increases so does the amount of alkali metal in the precipitate. Usually, and preferably, the alkali metal carbonate, bicarbonate and hydroxide are the sodium compounds. Other alkali metal carbonates and hydroxides can be used but are generally more costly. Ammonium carbonate and hydroxide may not be used because soluble ammine complexes are formed and ammonia is lost to the atmosphere; however, some ammonium ions can be tolerated in the solution of the water soluble salt, although there is some danger of ammine formation and loss of ammonia due to formation of the ammonia from the ammonium ions.

Maintaining the pH in the range 7.4 to 8.0, during the precipitation is essential. If the pH is too low, relatively large amounts of nickel remain in solution when addition of the sodium carbonate is complete. If the pH is too high, the filterability of the product is too low and alkali consumption is excessive. The precise physical and chemical nature of the precipitate can be adjusted for a given end use by adjusting the pH and temperature within the ranges used in the invention; further adjustment can be achieved by varying the agitation and aeration of the reaction and the precipitate slurry.

The following Examples illustrate the present invention. In the Tables runs designated

by numbers are Examples of the present invention whereas those designated by letters are comparative examples.

EXAMPLES 1 & 2.

The apparatus used consisted essentially of a cylindrical reaction zone, which was fitted to measure temperature and pH and contained an axially mounted turbine agitator and an aqueous reaction medium. Continuous agitated operation was established in this reaction zone by introducing a preheated metallurgical refinery sulphate leach solution containing about 20.1 gpl of nickel, about 7.2 gpl of cobalt, about 0.011 gpl of ferrous ion, about 0.60 gpl of calcium, about 0.077 gpl of magnesium, about 0.037 gpl of manganese and about 0.02 gpl of zinc and having a pH of 4.0 and preheated sodium carbonate solution. The reaction zone was aerated during the precipitation at about 1.5 reaction zone volumes per minute. After completion of the precipitation, the precipitate was aged by aeration for 10 minutes. The results obtained when the pH was maintained at 7.6 during the precipitation are given in Table I. The abbreviation " gpl " means grams per litre.

TABLE I

Run	1	2	H	I
Temperature (°C)	90	85	75	60
Precipitation time (mins.)	20	20	20	20
Na_2CO_3 % theoretical	101	102	106	107
Ageing time (mins.)	10	10	10	10
Settling rate (mph)	6.6	6.1	1.9	0.3
Under flow (% solids)	35	24	20	10
Filter rate ($1/m^2/hr$)	4700	5800	3330	2230
Filter cake (%) H_2O	47	44	69	78
Filter cake dry (%) Ni	37.0	34.4	35.1	35.1
Filter cake dry (%) Co	12.5	12.0	12.0	12.1
Mole ratio CO_3/ heavy metals	0.37	0.40	0.44	0.45
Filter cake dry (%) Na	0.015	0.013	0.015	0.041
Filter cake dry (%) S	0.55	0.76	0.33	0.27

In the Tables percentages are by weight, mph means metres per hour and $1/m^2/hr$ means litres per square metre of filter. hour.

The data in Table I show that, at temperatures below 85° C., the settling rate, the filter rate and the underflow solids content of basic metal carbonate precipitates formed at pH 7.6 are substantially less than the settling, filter rates and underflow solids content of basic metal carbonate precipitates formed at temperatures above 85° C. Chemical analysis of the relatively coarse products of the processes of Examples 1 and 2 shows the composition of the precipitate to be, in per cent by weight, 34 to 37% nickel, about 12% cobalt, about 0.7% calcium and less than 0.1% each of iron, magnesium, zinc and sodium. Only about 0.02 gram per litre of nickel and 0.008 gram per litre of cobalt remain in solution after the precipitation whereas about one-half the calcium and 0.7 of the magnesium originally present in the nickel feed solution remain in solution after

the precipitation. It should be noted that although precipitation was carried out at pH 7.6, aeration after the end of precipitation during ageing caused the pH to rise to 8.0 or higher.

EXAMPLES 3 to 5.

The effect of varying the pH at 90° C. is shown by the data in Table II, the same method being used as in Example 1.

TABLE II

Run	J	3	4	5	K
pH	7.4	7.6	7.8	8.0	8.5
Precipitation time (mins)	20	20	20	20	20
Na_2CO_3 (%) theoretical	98	102	106	111	144
Ageing time (mins.)	10	10	10	10	10
pH after ageing	7.8	8.0	8.3	8.5	8.7
Settling rate (mph)	4.2	6.1	6.1	6.1	3.8
Underflow (% solids)	27	25	25	25	28
Filter rate (1/m²/hr)	5570	6720	6300	5570	5570
Filter cake (%) H_2O	.53	51	51	49	59
Filter cake dry (%) Ni	34.8	37.3	37.9	38.0	38.1
Filter cake dry (%) Co	11.8	12.5	12.5	13.0	12.9
Mole ratio CO_3/ Heavy metal	0.38	0.38	0.41	0.38	0.35

The data in Table II show that relatively coarse basic carbonate precipitates formed at a pH in the range of 7.6 to 8.0 and about 90° C. have settling rates which are about 50% greater than settling rates of basic carbonates precipitated at the same temperature but at pH values slightly outside this range. Furthermore, the data show that precipitation at 90° C. in the more limited pH range of 7.6 to 7.8 results in enhanced filtering rates. All the products of Examples of the present invention shown in Tables I and II had mole ratios of CO_3 to total nickel, cobalt and iron of 0.37 to 0.41.

Additional tests at 90° C. and pH 7.7 using the same apparatus and reagents as used in the runs reported in Tables I and II indicate that in general too rapid addition of reactants, or, especially in a continuous process, too short a residence time in the reaction zone, can adversely affect the physical properties of the metal basic carbonate. For example, if the reaction time was reduced from 20 minutes to 5 minutes, during which time about 1 reaction zone volume of metal feed solution was introduced into the reaction zone with about one-quarter reaction zone of sodium carbonate solution, the more rapid addition reduced the precipitate settling rate from 4 to 6 metres per hour to a less satisfactory rate of about 0.6 metres per hour. Likewise, the filter rate of the slurry produced decreased substantially. Accordingly it is preferred to introduce the feed solutions slowly into the reaction zone. For example, solutions containing 10 to 50 gpl of precipitable metal should preferably be introduced no faster than about 6 reaction zone volumes per hour; in a continuous process using the same feed solutions it is preferred to maintain an average residence time in the reaction zone of at least 10 minutes. Using the feed solutions of the runs reported in Tables I and II the average residence time of metal in the reaction zone is preferably 10 to 25 minutes, for example about 13 minutes, so as to give a precipitate settling rate of at least 5 metres per hour.

EXAMPLE 6.

The reactor used comprised a baffled reaction zone, measuring devices for temperature

and pH, an agitator, means for heating the feeds and an overflow. This reactor was operated continuously at pH 7.7 and 90° C. to provide a relatively coarse product continuously. The feed inlets for metal and carbonate solutions were on opposite sides of a flat blade turbine impeller of the agitator. The metal feed comprised an aqueous sulphate solution containing 20 gpl of nickel, 0.5 gpl of cobalt and 10 gpl of sodium. The car-

bonate feed comprised a 220 gpl aqueous solution of sodium carbonate. Metal residence time in the reaction zone was about 21 minutes. Table III contains data on the product produced by operating the reactor without aeration for the times indicated; these data show the suitability of the process of the present invention for continuous operation.

TABLE III

Sample No.	Time Mins.	Settling Rate (mph)	Underflow Solids (%)	Filter Rate l/m².hr	Filter Cake H₂O (%)	Filter Cake (dry) % Ni	Co	Na	S	CO₃	OH	H₂O	CO₃/(Ni + Co) molar
1	15	4.5	—	6900	59	41.2	1.26	0.11	0.21	20.6	12.8	23.4	0.47
2	45	5.4	33	6500	44	42.0	1.26	0.22	0.21	24.0	14.4	20.5	0.42
3	75	4.8	32	6700	46	41.5	1.23	0.16	0.19	23.6	11.3	21.6	0.54
4	105	7.1	41	6700	29	40.7	1.22	0.71	0.39	25.2	10.7	20.3	0.59
5	135	5.2	34	5900	42	40.0	1.24	0.52	0.30	24.0	10.4	22.9	0.57
6*	165	6.9	41	6200	30	40.3	—	0.33	0.30	23.3	10.8	23.2	0.55
7*	225	5.7	28	6300	49	39.7	—	0.37	0.27	23.5	10.4	24.0	0.56
8	255	4.8	26	6000	52	40.0	0.86	0.15	0.23	22.4	10.9	25.0	0.55
9	285	4.7	26	6100	43	40.3	—	0.08	0.15	22.1	11.3	24.9	0.53
10	315	4.2	27	—	48	39.6	—	0.12	0.17	22.2	10.8	25.9	0.53
11	360	4.1	30	6300	42	41.4	0.89	0.10	0.22	22.8	11.4	22.7	0.53
12	390	4.8	24	5400	47	39.2	—	0.08	0.18	21.1	11.1	27.1	0.51

* Agitator motor operating at 850 rpm reduced speed between Samples 6 and 7 to 500 rpm. Operation was halted for a few minutes to change the motor.
— not determined.

Details of other Examples of the process of the present invention are set out in Table IV.

TABLE IV

Example No.	7	8	9	10
Metal Feed Sol				
Ni++ gpl	0.1	0.06	29.8	29.8
Co++ gpl	50	53.4	0.51	0.51
Anion	Sulphate	Sulphate*	Sulphate	Sulphate
NH$_4$+ gpl	—	—	10.6	10.6
pH	2.5	Acid	4.1	4.1
Carbonate Solution				
Na$_2$CO$_3$ (gpl)	350	250	350	280
NaOH (gpl)	—	—	—	53
Reaction Conditions				
Agitation	yes	yes	yes	yes
pH	7.6	7.7—7.8	7.9	7.9
Aeration	yes	no	yes	yes
Time (minutes)	18	continuous**	—	—
Temperature (°C)	90	90	90	90
Slurry Characteristics				
Settling Rate (mph)	76	9	3.1	1.5
Underflow (% Solids)	34	70	34	23
Filter Rate (l/m²/hr)	10,400	10,000	—	—
Filter Cake % H$_2$O	33	11—15	47	65
Filter Cake (dry) % Co	54.0	43.5	.81	.80
Filter Cake (dry) % Ni	—	.076	48.0	47.6
Filter Cake (dry) % Na	.076	3.75	.016	.036
Filter Cake (dry) % S	.14	.045	.21	.60
Filter Cake (dry) % CO$_3$	24.1	32.2	21.4	18.8
Filter Cake (dry) % OH	17.5	9.7	—	—
Filter Cake (dry) % NH$_3$	—	—	.66	.75
Mole Ratio CO$_3$/Co	.44	.73·	.43	.38

* includes small amounts of calcium and magnesium and 9.7 gpl of free H$_2$SO$_4$

** residence time about 20 minutes

— not determined.

WHAT WE CLAIM IS:—

1. A process for preparing a precipitate of carbonate or basic carbonate of nickel, cobalt, copper or zinc in which a stream of a first aqueous solution of a water soluble salt of nickel, cobalt, copper or zinc is mixed substantially continuously in an agitated reaction zone at a temperature in the range of from 85 to 95° C. and at a pH in the range of from 7.4 to 8.0 with a stream of a second aqueous solution of an alkali metal carbonate, an alkali metal carbonate and hydroxide or an alkali metal carbonate and bicarbonate, and the resulting precipitate is recovered, the amount of alkali metal carbonate and hydroxide or bicarbonate, expressed in terms of the alkali metal, being that required to use up any free acid in the salt solution and additionally from 100 to 127% of the theoretical stoichiometric amount required to precipitate the pure normal carbonate.

2. A process according to claim 1 wherein the water soluble salt is a salt of nickel or cobalt or a mixture thereof.

3. A process according to claim 1 or 2

wherein the temperature is about 90° C.

4. A process according to any one of the preceding claims wherein the pH is in the range of from 7.6 to 7.8.

5. A process according to any one of the preceding claims wherein the water soluble salt is a sulphate.

6. A process according to any one of the preceding claims wherein the reaction zone is aerated during precipitation.

7. A process according to any one of the preceding claims wherein the precipitate is in the form of a slurry and the slurry is aerated.

8. A process according to any one of the preceding claims wherein the second aqueous solution is a solution of sodium carbonate and sodium hydroxide in which the mole ratio of sodium hydroxide to sodium carbonate is up to 2:1.

9. A process according to claim 1 substantially as hereinbefore described.

10. A process according to claim 1 substantially as described in any one of the foregoing Examples.

11. A basic carbonate of nickel, cobalt, copper or zinc when prepared by a process according to any one of the preceding claims.

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